

REFRATORIES FOR THE GLASS INDUSTRY

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THERMOPHYSICAL CHARACTERISTICS OF REFRACTORY COMPOSITE MATERIALS FOR GLASS PRODUCTION

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When a lining consisting of large refractory parts is put into a working regime, it is important to know the increase in the temperature of the material in order to determine the assembly gaps and be confident that fracture as a result of structural transformations will not occur during operation when the temperature gradient over the thickness of a part increases. Comparative studies of the thermophysical properties of conventional fired fireclay materials (tamped beam for the bottom of the melt tank, semi-dry pressed ShSU beam) and low-cement concrete materials with VShS fireclay filler have been performed at the Semiluki Refractory Works. The materials BShBS and VShBO showed negligible change of the CLTE with increasing temperature in the operating range 600 – 1300°C.

There are indisputable advantages to using refractory concrete parts in the lining of commercial high-productivity furnaces for producing glass. First and foremost, these are great freedom in designing parts with different shapes and sizes, fewer seams in the refractory masonry because large beams are used, mechanization, and continuity of the assembly of the lining as a result of the accuracy of the geometric dimensions of even the largest parts.

In spite of all this, however, the main user problem, which, as a rule, arises because of the properties of the binding system of composite materials such as low-cement concrete, is obtaining the correct setting of the apparatus governing the heat – moisture regime when a lining made of unfired concrete parts is put into and taken out of the working regime, since the heat-treatment temperature for such parts at the manufacturer does not exceed 400°C.

Characteristically, when a refractory material is heated its volume changes: a temporary change, which vanishes on cooling, as a result of the thermal expansion of the material and a residual change which occurs as a result of chemical and physical transformations and, as a rule, happens when the operating temperature of the material is higher than the firing temperature of the material or when during firing of

the part the required holding time at maximum temperature was not reached. The character of the volume changes depends on the nature of the refractory material. Thus, positive growth is characteristic for dinas-clay parts and negative growth is characteristic for fireclay parts.

When equipment lined with large parts, such as the bottom beam in a glass-making furnace and the beam for the lining at the bottom of the tin melt tank, is put into a working temperature regime, it is very important to know the growth indicator for the material in all directions in order to determine the assembly gaps and be confident that the masonry will not fail as a result of structural transformations during operation with an increase of the temperature gradient over the thickness of the part. Conventionally, such parts have been made of fireclay by manual tamping or semi-dry pressing followed by firing up to a temperature of at least 1300°C.

For refractory parts to be used in the lining of a float tank, it is also necessary to combine low permeability for gases and tin, i.e., low open and channel porosity, with good thermal stability and the required thermal conductivity, since the temperature differential over the thickness of the refractory masonry at the bottom reaches 800°C.

It is known that the proneness of a refractory to crack during temperature changes is a direct function of the CLTE and an inverse function of elasticity and thermal conductivity [1].

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While the CLTE and thermal conductivity are determined by the composition of the material, the elasticity depends on its structure, and the particle size and the particle-size distribution have a large effect. Parts with the highest elasticity consist predominantly of large filler particles bound a soft binder with small pores. Coarse-grain material has not only twice the resistance to cracking compared with a fine-grain material but it also shrinks less when dried and fired, its compression is smaller under a low and high temperature, and its thermal conductivity is lower. In this connection, composite materials such as low-cement refractory concretes can be modified to meet the requirements for the lining precisely because of the method of vibrational shaping and the multivariate composition of the binder. The increase in the heat resistance of hydration-hardened concretes is due to the decrease of the intensity of destructive processes during recrystallization and dehydration of calcium hydroaluminates as well as formation of thermally stable refractory compounds in the products of firing [2].

High density and strength of refractory material are accompanied by higher thermal conductivity. On the one hand, the thermal resistance of the part increases but on the other hand high conductivity signifies high heat transfer, which inevitably results in an increase of the temperature of the exterior surface of the thermal equipment. This is inadmissible for a glass-making furnace and for the bottom of a tin melt tank, especially in the latter case, when the temperature of the outer surface of the lining of the melt tank must not exceed a prescribed value.

In the present investigation, the thermophysical properties of concrete materials, developed at the Semiluki Refractory Works for lining of the bottom of a glass-making furnace and the tin melt tank of a float-line for producing glass, are studied.

It is known that the properties of large tamped and pressed parts are anisotropic over thickness and depend on the direction of application of the shaping load. Concrete parts, because of vibrational shaping, should not show such variation. For vibrational compaction, the irreversible deformation and, ultimately, the density of the layer of the material formed are determined primarily by structural deformation. Plastic deformation and brittle fracture of particles either do not occur or are negligible so that they have no appreciable influence on the course of the process. Comparative studies of the thermophysical properties of conventional fired fireclay materials were performed to develop new concrete materials: tamped beam for the bottom of the melt tank (bottom beam), semi-dry pressed ShCU beam, and low-cement concrete materials based on VShS fireclay filler (below — VShS-2, VShBS, BShBO).

The thermal expansion indicators (the relative elongation ε and CLTE α in a prescribed interval of the temperature t) were determined with a DIL 402C (NETZSCH-Gerätebau GmbH (Germany)) high-temperature automatic horizontal dilatometer.

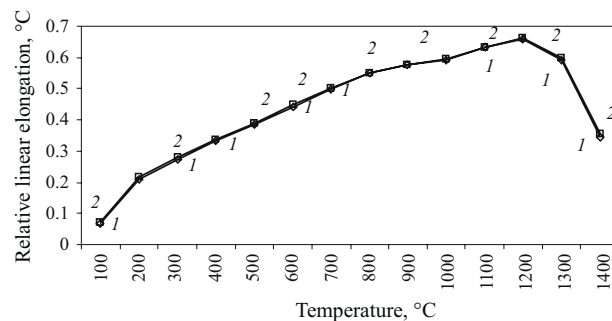


Fig. 1. Relative linear elongation of samples of VShBS material, determine parallel (1) and perpendicular (2) to the length of the sample.

The relative change of the length of the sample (%) $\varepsilon(t)$ in the temperature interval $t_0 - t$ was calculated from the formula

$$\varepsilon(t) = \frac{\Delta L_s}{L_{0,s}} \cdot 100,$$

where ΔL_s is the absolute change of the length of the sample in the temperature interval $t_0 - t$ taking account of corrections, mm, and $L_{0,s}$ is the length of the sample at the initial temperature t_0 , mm.

The CLTE (K^{-1}) $\alpha(t)$ in the temperature interval $t_0 - t$ was calculated from the formula

$$\alpha(t) = \frac{\Delta L_{0\delta p}}{L_{0, \delta p} (t_0 - t)}.$$

Measurements of $\varepsilon(t)$ and $\alpha(t)$ for concretes were performed in the temperature interval 30 – 1500 °C with the heating rate 10 K/min in an oxidative static medium (air) on samples in the form of rectangular parallelepipeds with cross-section 5 – 6 mm and length 24 – 26 mm cut out in two perpendicular directions to reveal property anisotropy. No anisotropy of the linear expansion of the VShBS material was found — in Fig. 1 the curves of the relative linear expansion virtually coincide. Consequently, further investigations of these samples were performed in one direction perpendicular to the length of a cylinder.

At temperatures up to 300 °C the values of the linear elongation of all samples are virtually the same (Fig. 2), but for concrete samples the elongation occurring with increasing temperature is much smaller, especially compared with the bottom beam, and its value is even smaller for the experimental sample VShBS-2 whose composition is under development.

The values of the CLTE for concrete samples also favor the materials presented; they are less than for the ShSU beam — the profile of the curves is similar (Fig. 3). The materials VShBS and VShBO showed a smooth negligible change of

TABLE 1.

Indicator	Parts				
	concrete			fired	
	VShBS	VShBO	VShS-2	ShSU beam	bottom beam
Mass fraction, %:					
Al ₂ O ₃	43.75	42.25	43.03	34.40	30.80
Fe ₂ O ₃	1.22	1.19	1.16	1.62	0.98
CaO	1.98	1.88	2.05	—	—
Apparent density, g/cm ³	2.19	2.15	2.15	2.10	2.08
Open porosity, %	18.8	18.4	19.8	16.6	14.6
Ultimate compressive strength, N/mm ²	45.8	43.3	42.6	44.6	52.4
Thermal conductivity, W/(m · K), at temperature 500°C	1.19	1.15	1.13	1.19	1.21
Residual linear changes, %, at temperature 1000°C	−0.1	0.0	−0.1	0.0	0.0
Thermal stability, number of temperature changes (950°C – water)	15	18	15	10	12

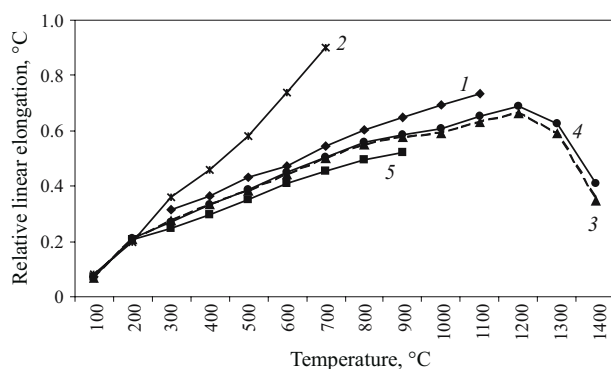


Fig. 2. Relative linear elongation of fired samples — ShSU beam (1), bottom beam (2), concrete materials VShBS (3), VShBO (4), and VShS-2 (5).

the CLTE with increasing temperature in the operating temperature range 600 – 1300°C.

The properties of the materials investigated are presented in Table 1.

Even though the concrete materials have a somewhat higher content of aluminum oxide, their thermal conductivity is comparable to and even somewhat lower than that of fired fireclay parts.

The data obtained clearly show that thermophysical characteristics of unfired parts made of the concrete materials developed at the Semiluki Refractory Works are at least as good as those of conventional fired materials. As a result of the low values of the linear elongation, VShBO and VShBS concrete parts have an advantage as structural materials over fired tamped beams. The variation of the CLTE with increasing temperature supports the fact that the risk of failure of the

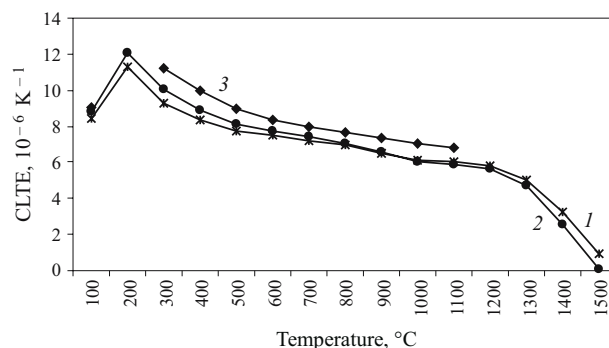


Fig. 3. Variation of CLTE of the concrete materials VShBO (1), VShBO (2), and ShSU beam (3) at elevated temperature.

masonry with repeated heating is reduced to a minimum. The temperature differential over the thickness of unfired parts made of VShBO and VShBS materials does not cause them to fail as they are put into the working regime.

The variation of the characteristics investigated with increasing temperature for unfired materials is similar to that of fired materials. Therefore there are no grounds for a substantial re-examination of the schedule for bringing thermal equipment to working temperatures.

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